Isotopic composition of nitrate in the Illinois Waterway

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- Mike Sopcak and his team for sample collecting
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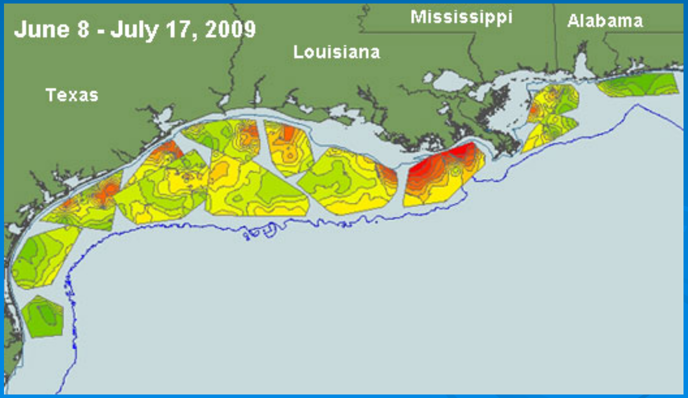
- MWRDGC for financial support

Why is Nitrate Important?

- Health effects:
  - EPA limit = 10 mg/L NO_3-N
  - Birth defects
  - Blue baby syndrome (methemoglobinemia)
  - Possible carcinogen

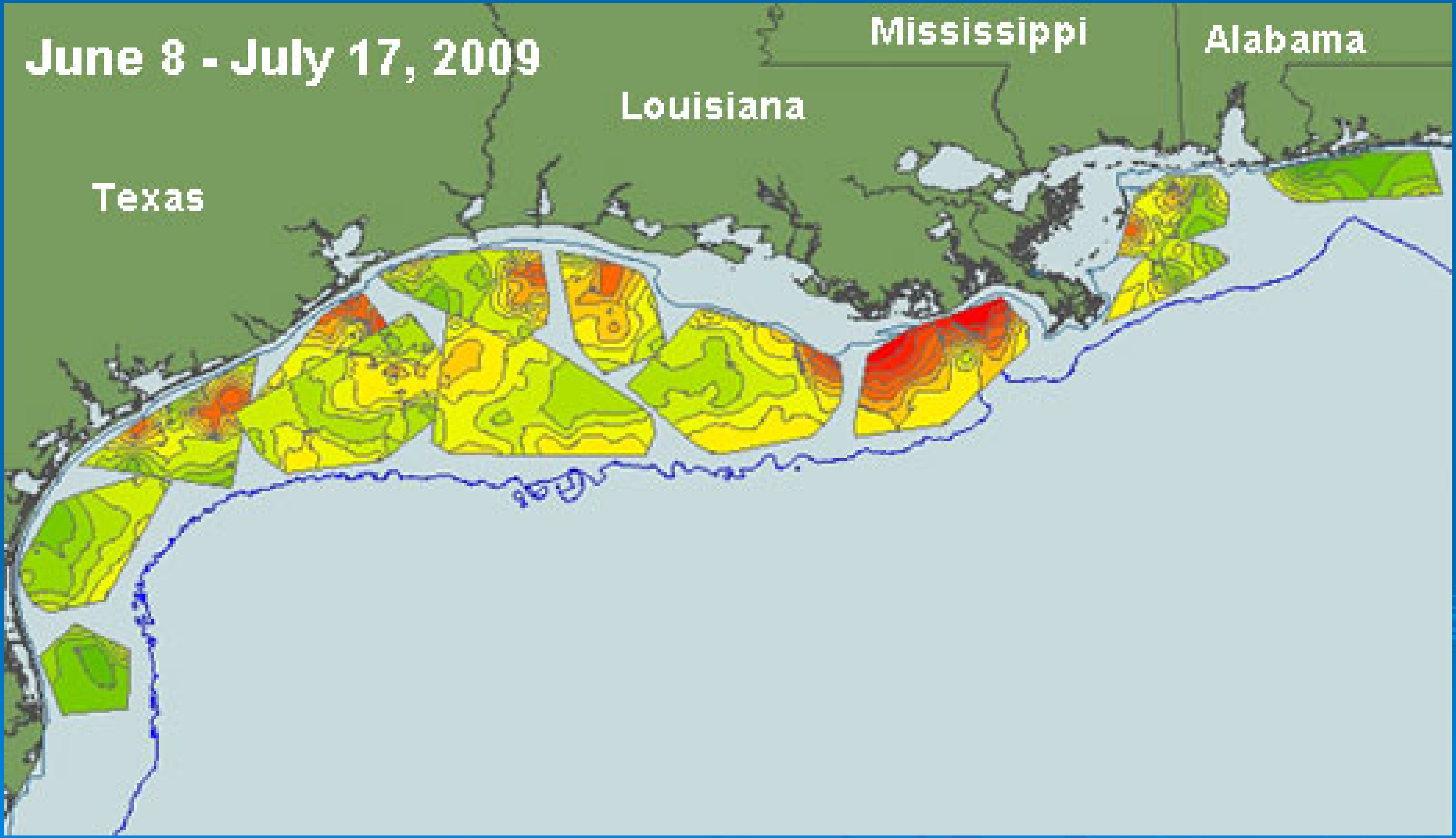
- Environmental effects:
  - Hypoxia and eutrophication
  - Dead zone in Gulf of Mexico



Nitrate sources

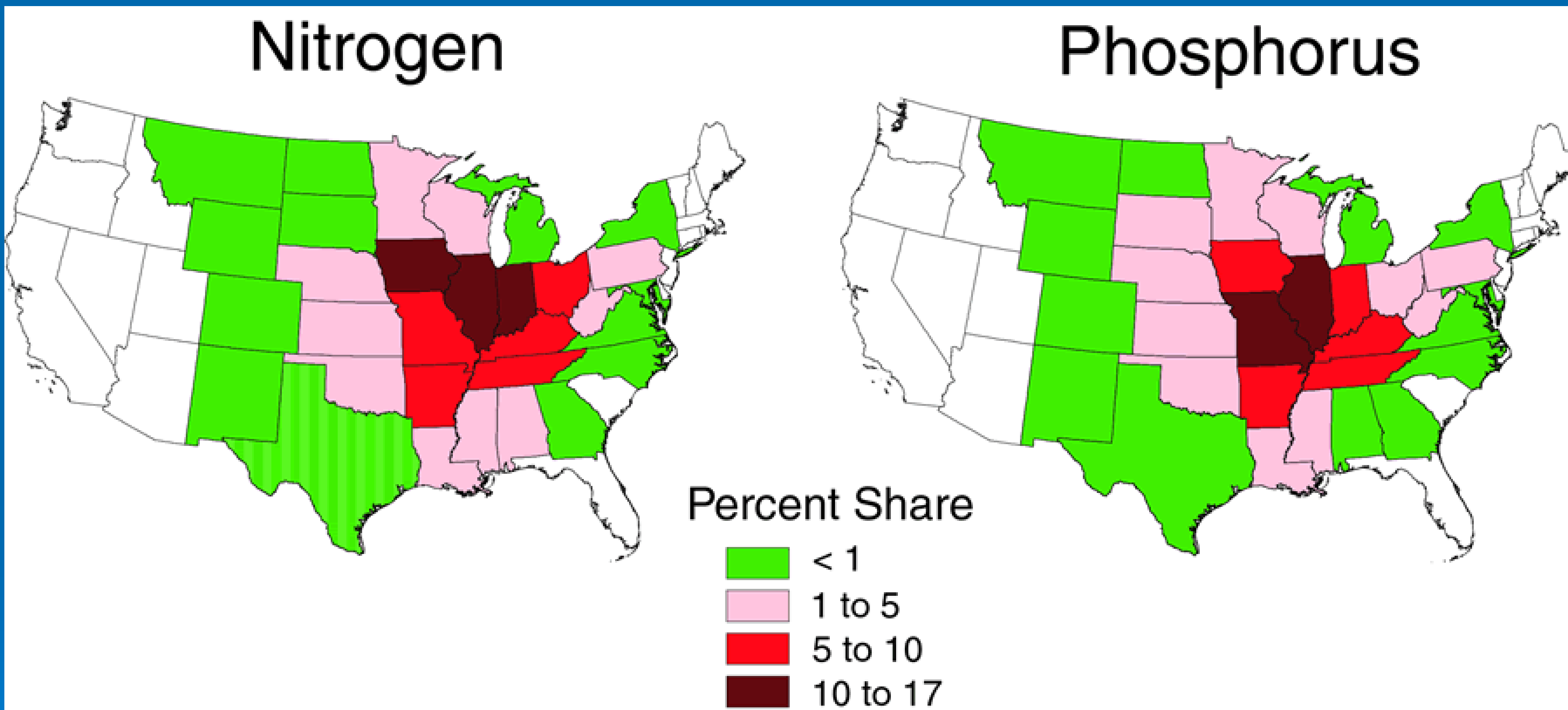
- Fertilizers
- Animal waste
- Septic systems
- Municipal sewage treatment plants
- Decaying vegetation

Gulf of Mexico hypoxia



http://ecowatch.ncddc.noaa.gov/hypoxia

Nutrient contributions to the Gulf, by State



http://water.usgs.gov/nawqa/sparrow/

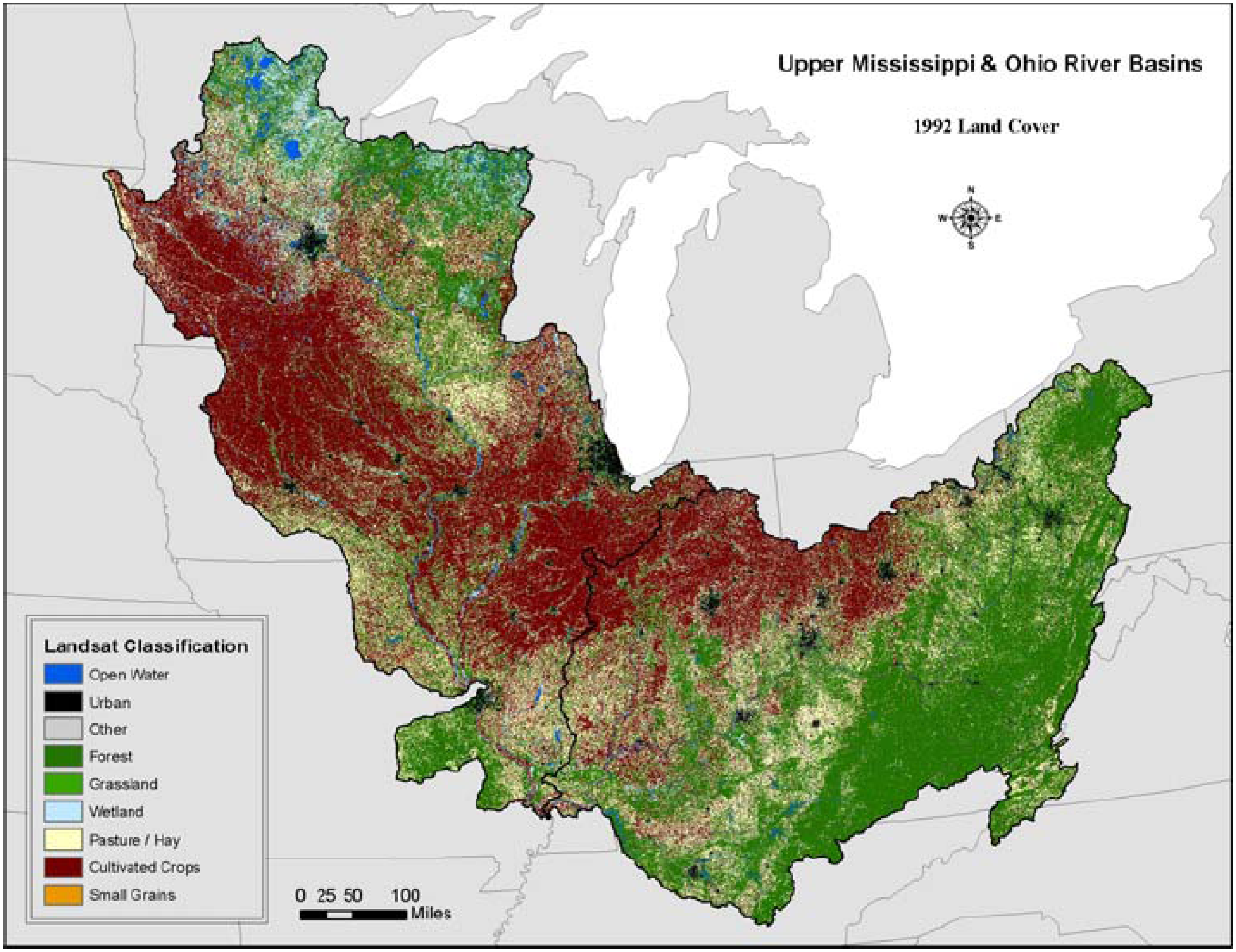


Figure 11: Land cover based on Landsat data (adapted from Crumpton et al., 2006).

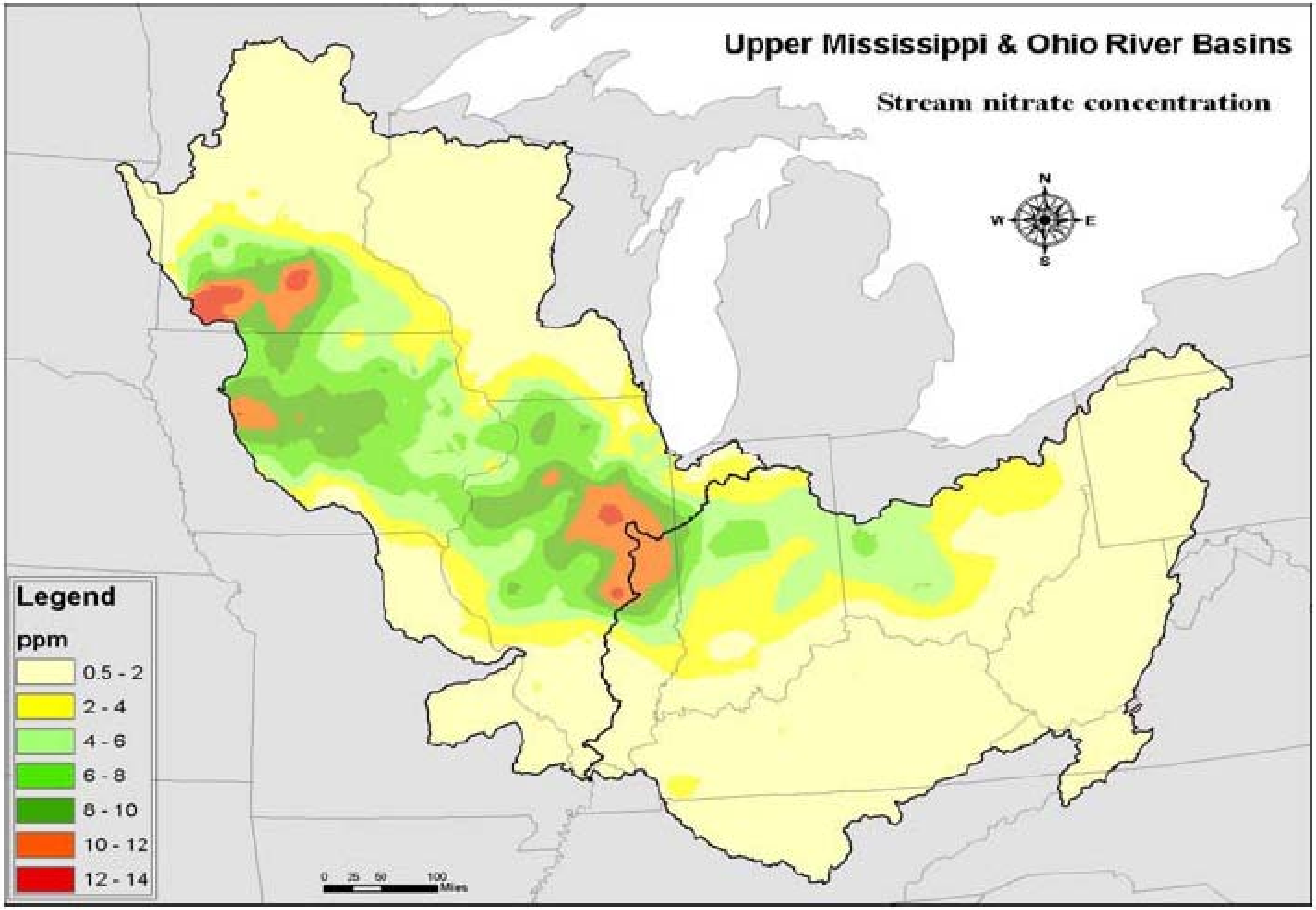


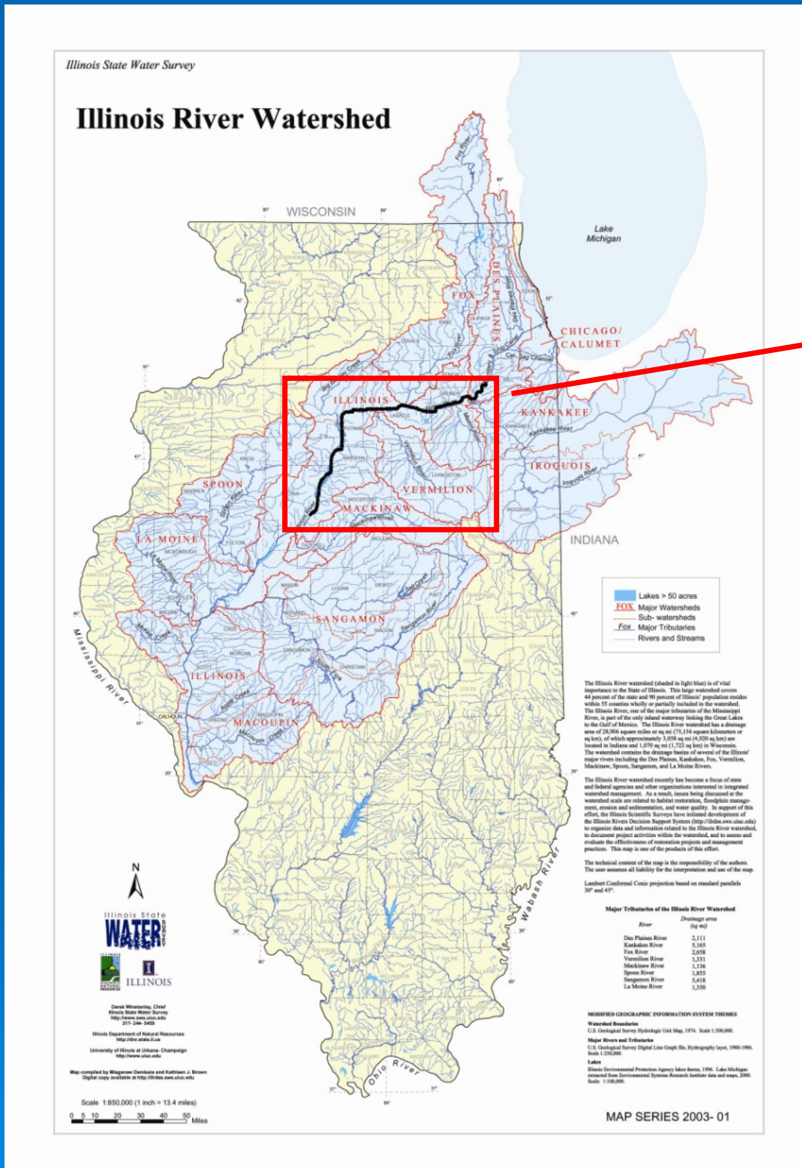
Figure 12: Flow weighted average nitrate concentrations estimated from STORET data selected to exclude point source influences (adapted from Crumpton et al., 2006).

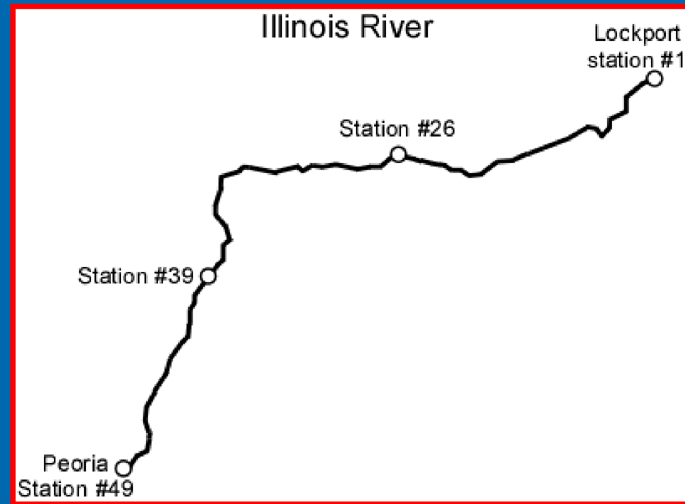
Table 1. Top 10 States Contributing Nitrogen to the Gulf of Mexico

#	State	% of Total Nitrogen Contribution to Gulf
1	Illinois	16.8%
2	Iowa	11.3%
3	Indiana	10.1%
4	Missouri	9.6%
5	Arkansas	6.9%
6	Kentucky	6.1%
7	Tennessee	5.5%
8	Ohio	5.4%
9	Mississippi	3.4%
10	Nebraska	3.2%

Source: Alexander et al., 2008.

Study Site





- Samples were taken at all 49 stations along the Illinois River waterway from Lockport to Peoria in October 2004, May 2005, August 2005 and October 2005.
- Monthly samples were taken at stations #1, 4, 8, 20, 23, 30 and 39, March through October 2006
- Monthly samples were taken at stations #1, 4, 8, 20, 30, 39, and 46, and at eight tributary streams and Senachwine Lake, March through October, 2008.

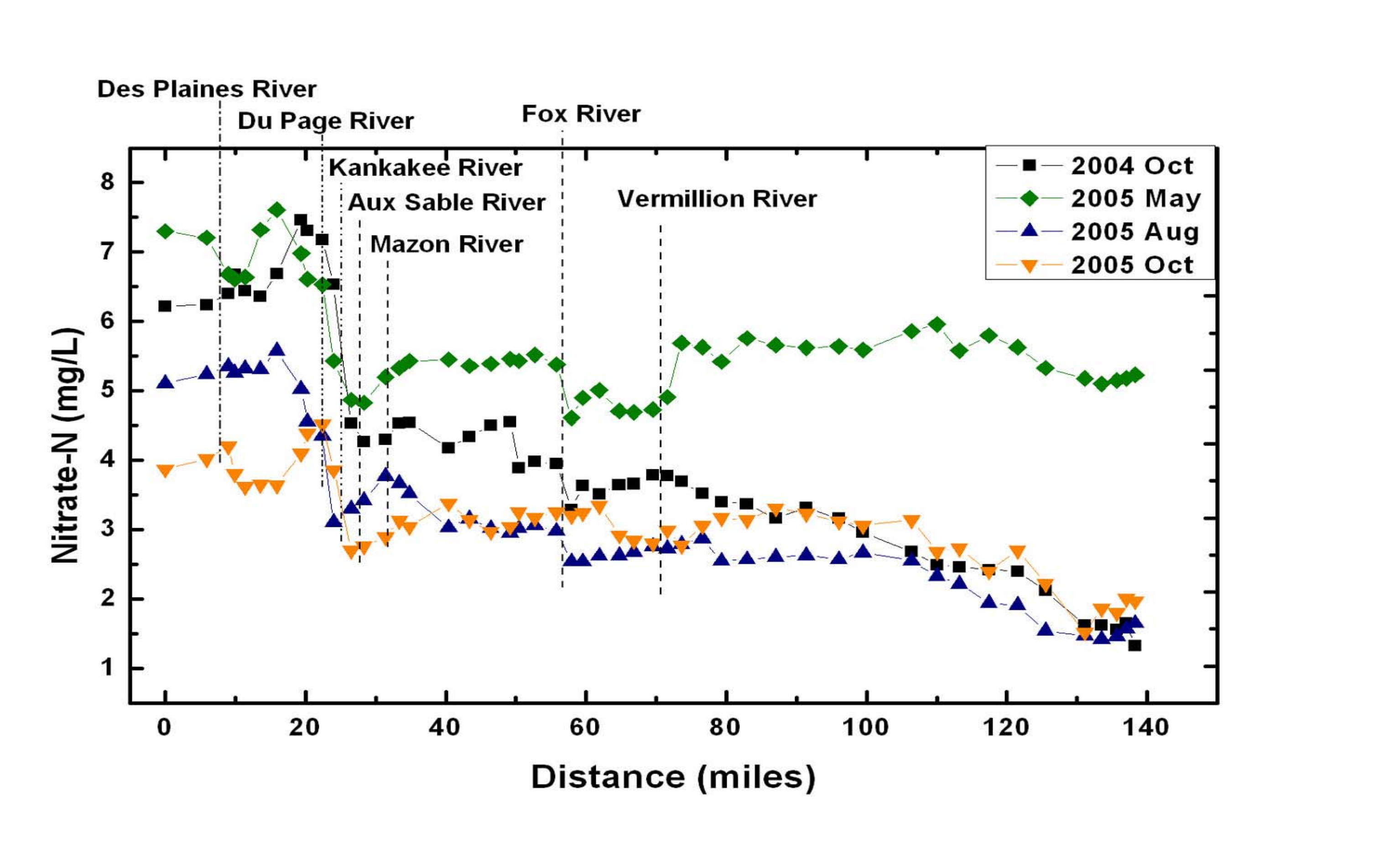
Objectives of Illinois Waterway Study

- Determine if different sources of nitrate have different isotopic characteristics, and if so, can isotopic data be used for tracking nitrate in the waterway?

- Relate isotopic data to nitrate fluxes and constrain the relative importance of different nitrate input and removal mechanisms (e.g. soil flushing, plant uptake, denitrification)

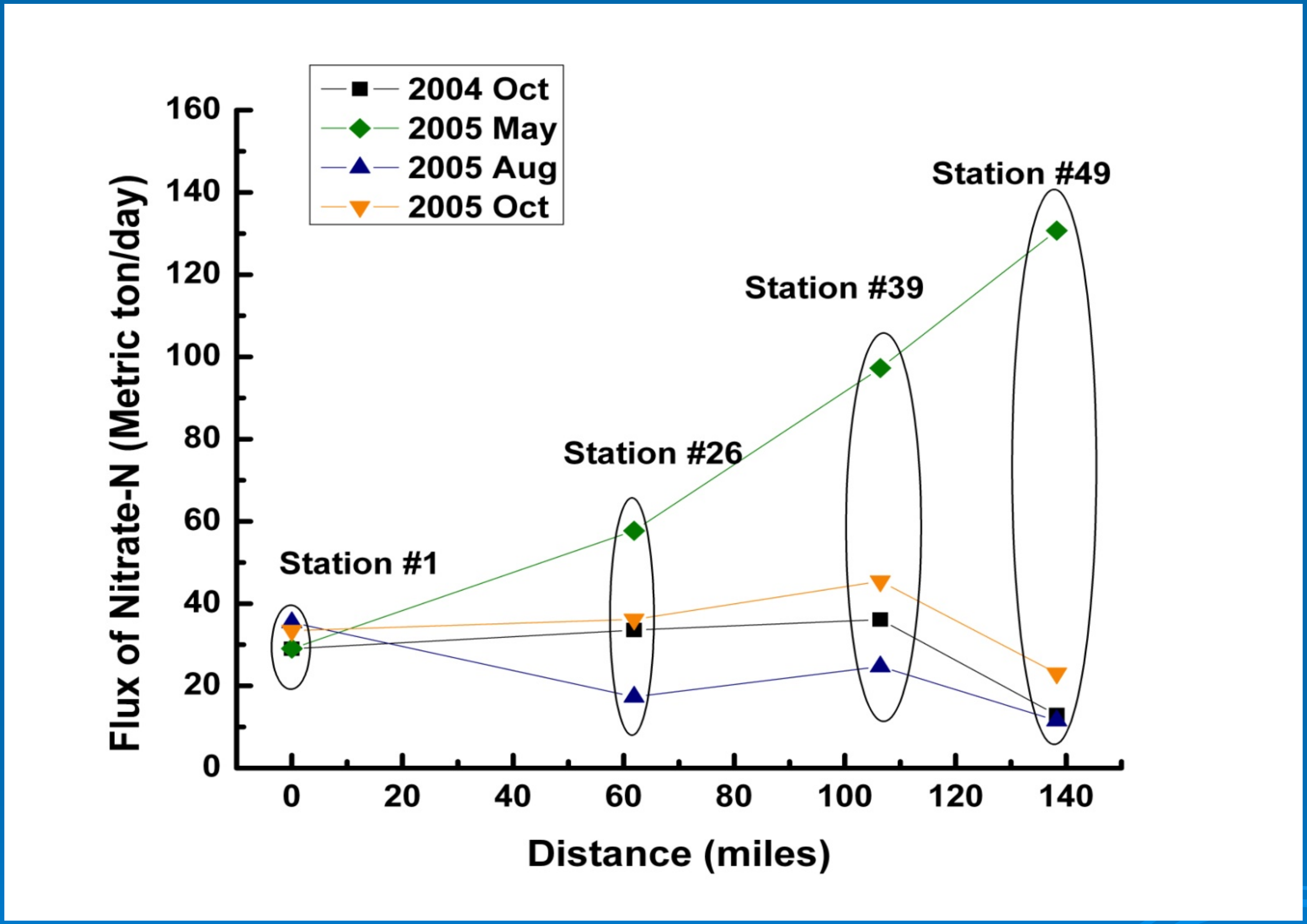
Results

Nitrate concentration data - 2005



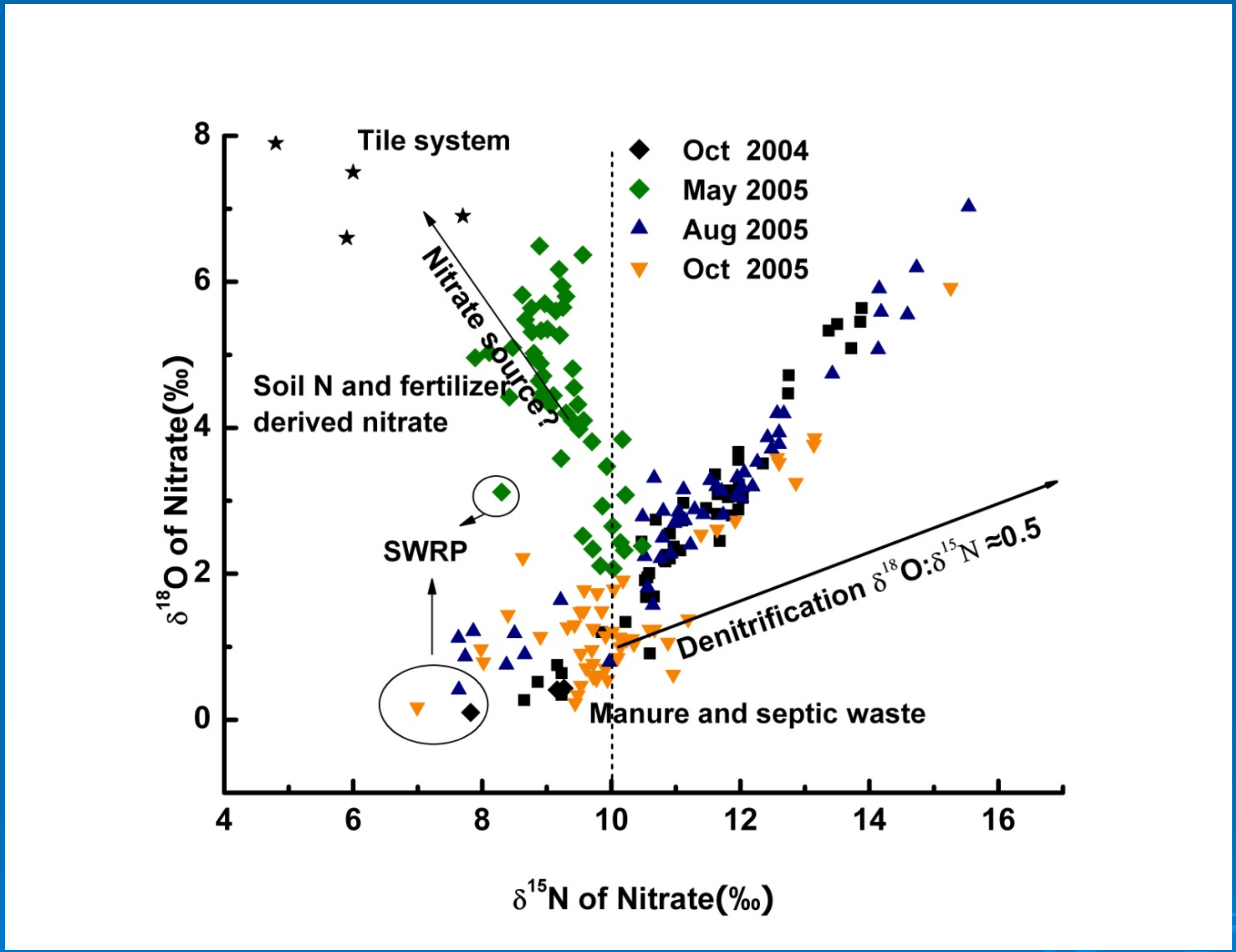
Nitrate concentration with distance along the waterway in quarterly samples from 2004-2005

Nitrate flux data - 2005



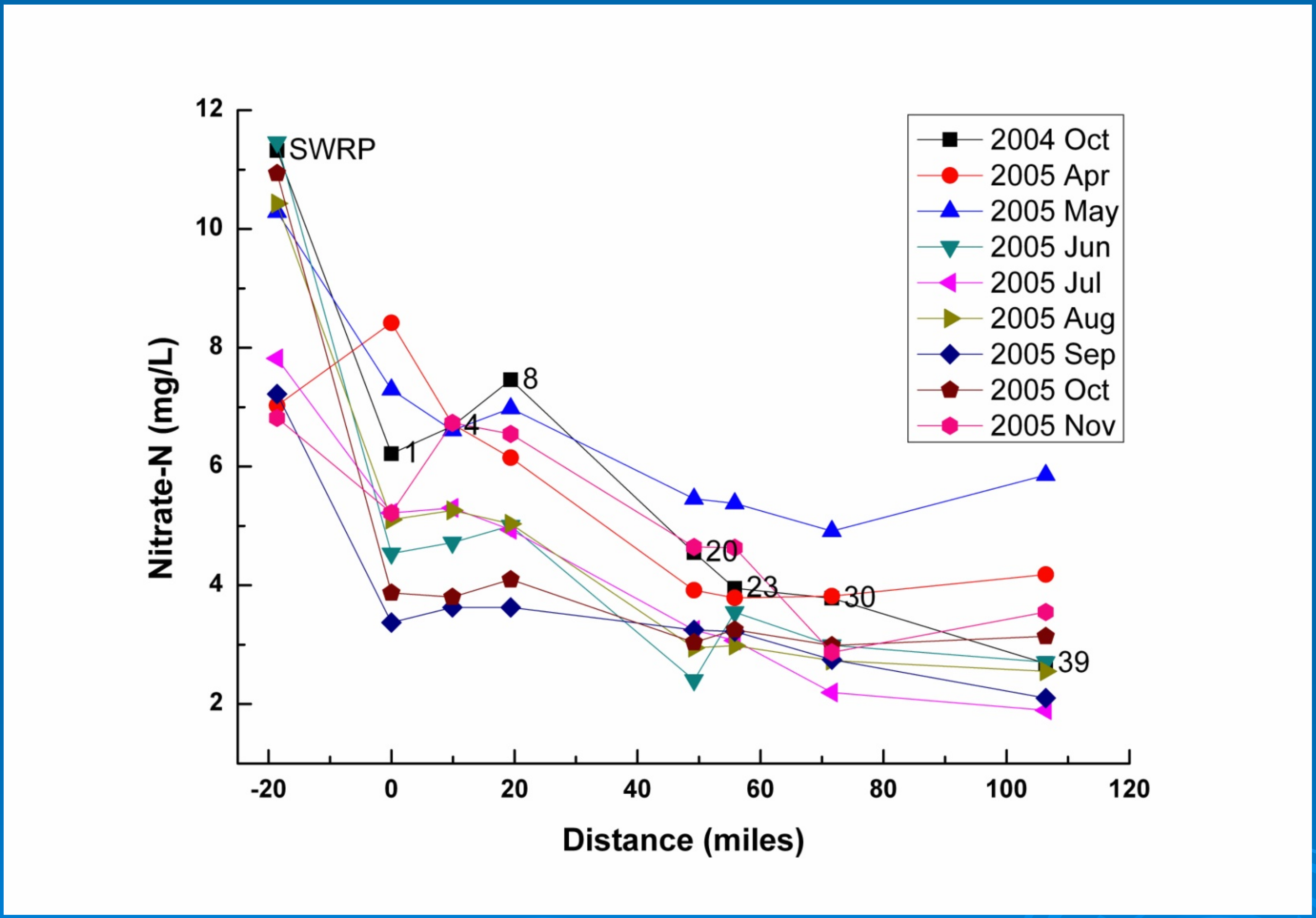
Nitrate flux changes with distance along the Illinois River waterway in 2004-2005

Isotopic data - 2005



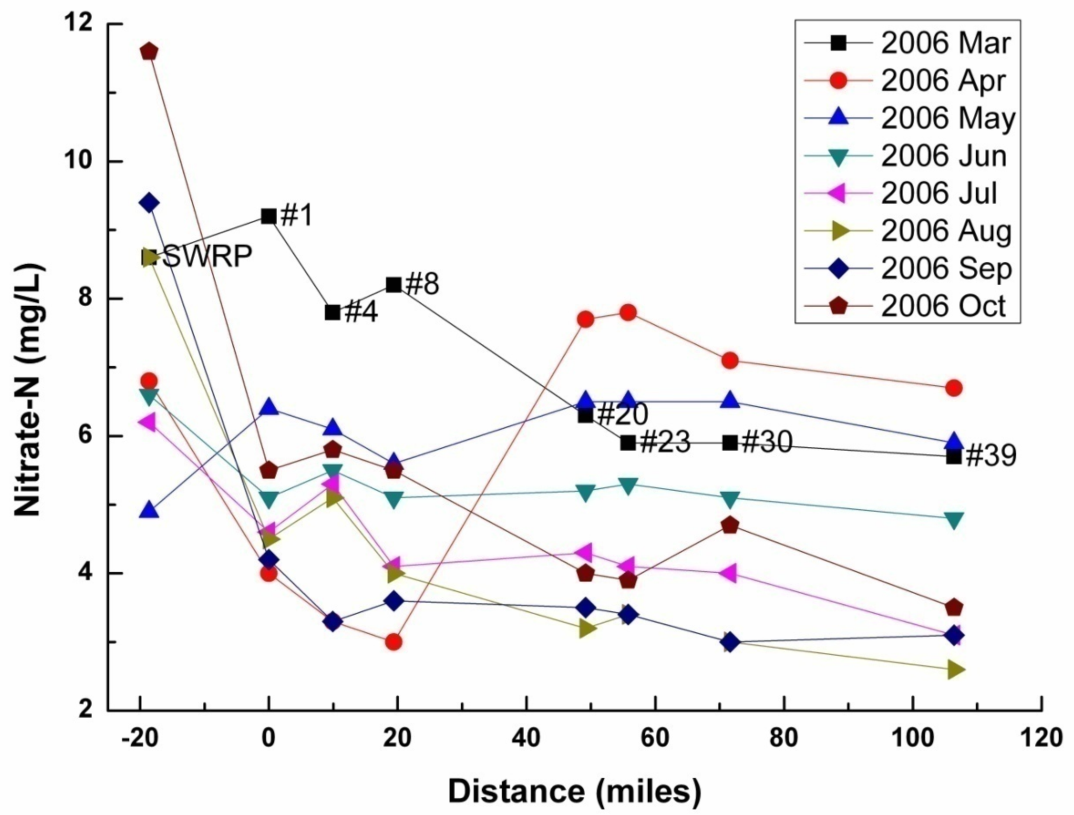
Detail of previous figure. Data also shown for samples from tile drainage systems during spring (stars, from Panno et al., 2006). SWRP is Stickney Water Reclamation Plant effluent.

Nitrate concentration data – 2005 monthly



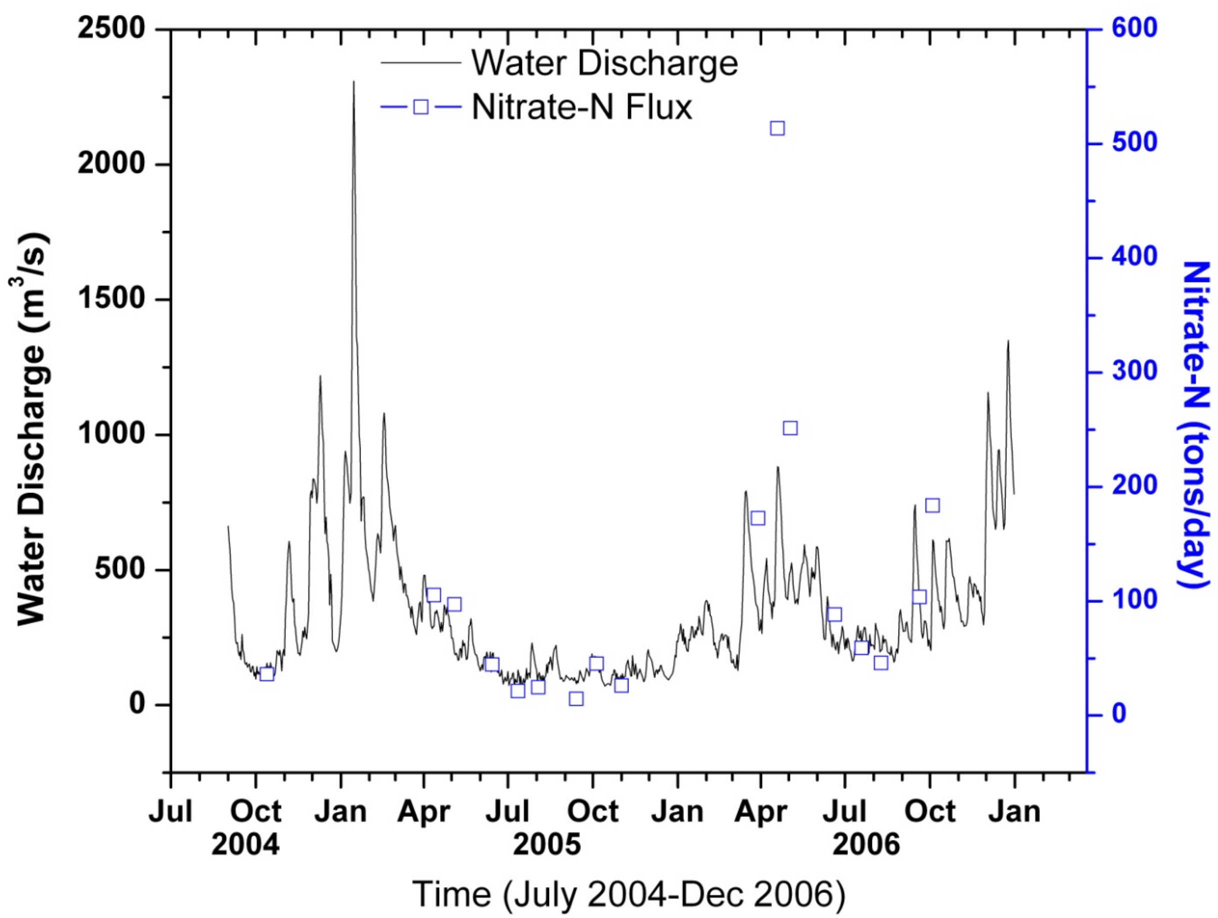
Nitrate concentration with distance along the waterway in monthly samples from 2005

Nitrate concentration data – 2006 monthly



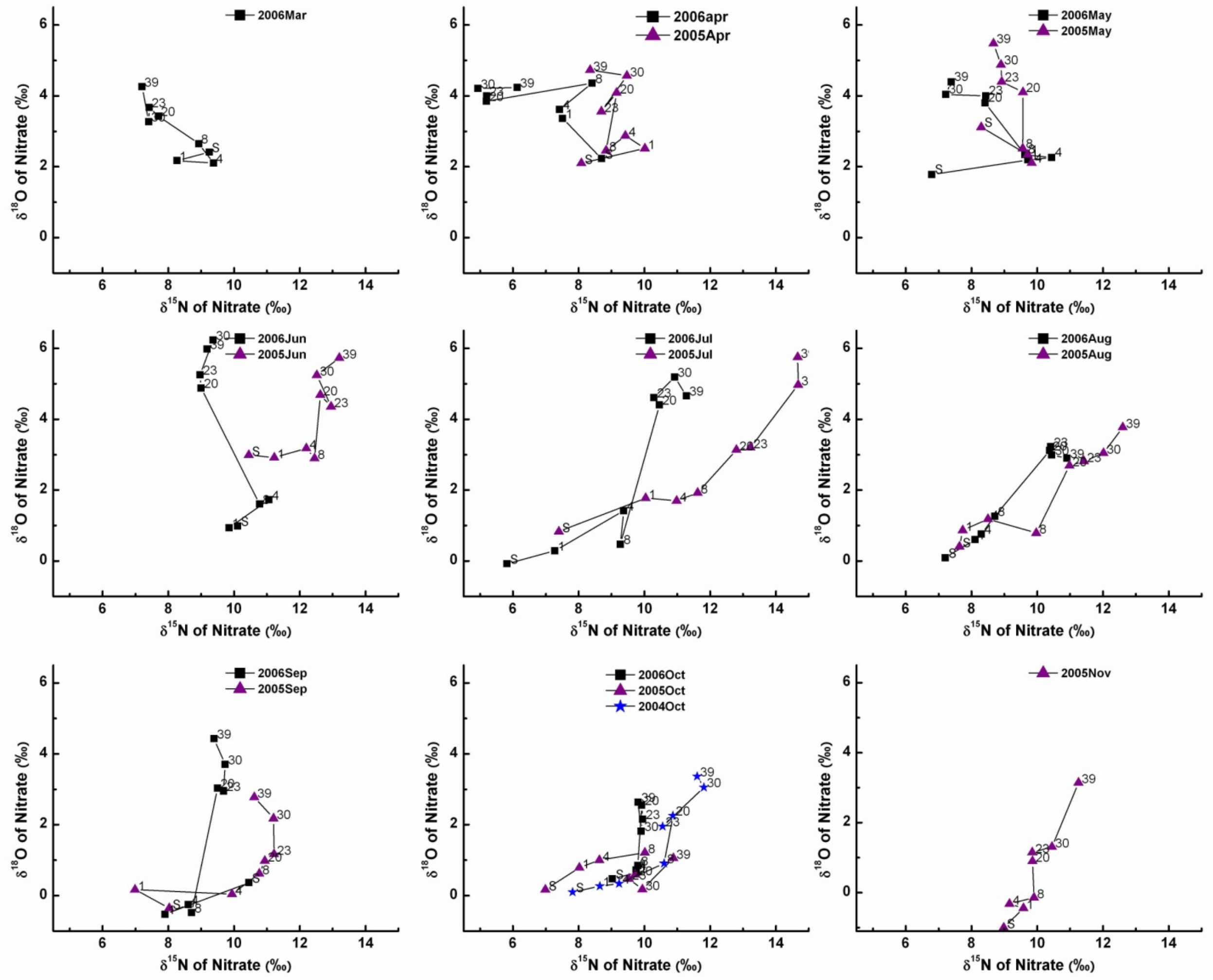
Nitrate concentration with distance along the waterway in monthly samples from 2006

Nitrate flux data 2005-2006



Correlation of nitrate flux with discharge at station #39 (Henry, IL), October 2004-October 2006

Monthly nitrate isotopic data comparison: 2005-2006



Summary of 2006 Results

- During 2006, overall patterns of nitrate concentration and isotopic composition were similar to those observed during 2004-2005.

- Isotopic data for nitrate indicate that the extent of apparent downstream denitrification ($\delta^{15}N > 10$ ‰) was less during 2006, and the influence of agricultural nitrate was observed for a longer period.

- Nitrate flux is strongly correlated with discharge over entire 2004-2006 period of observation.

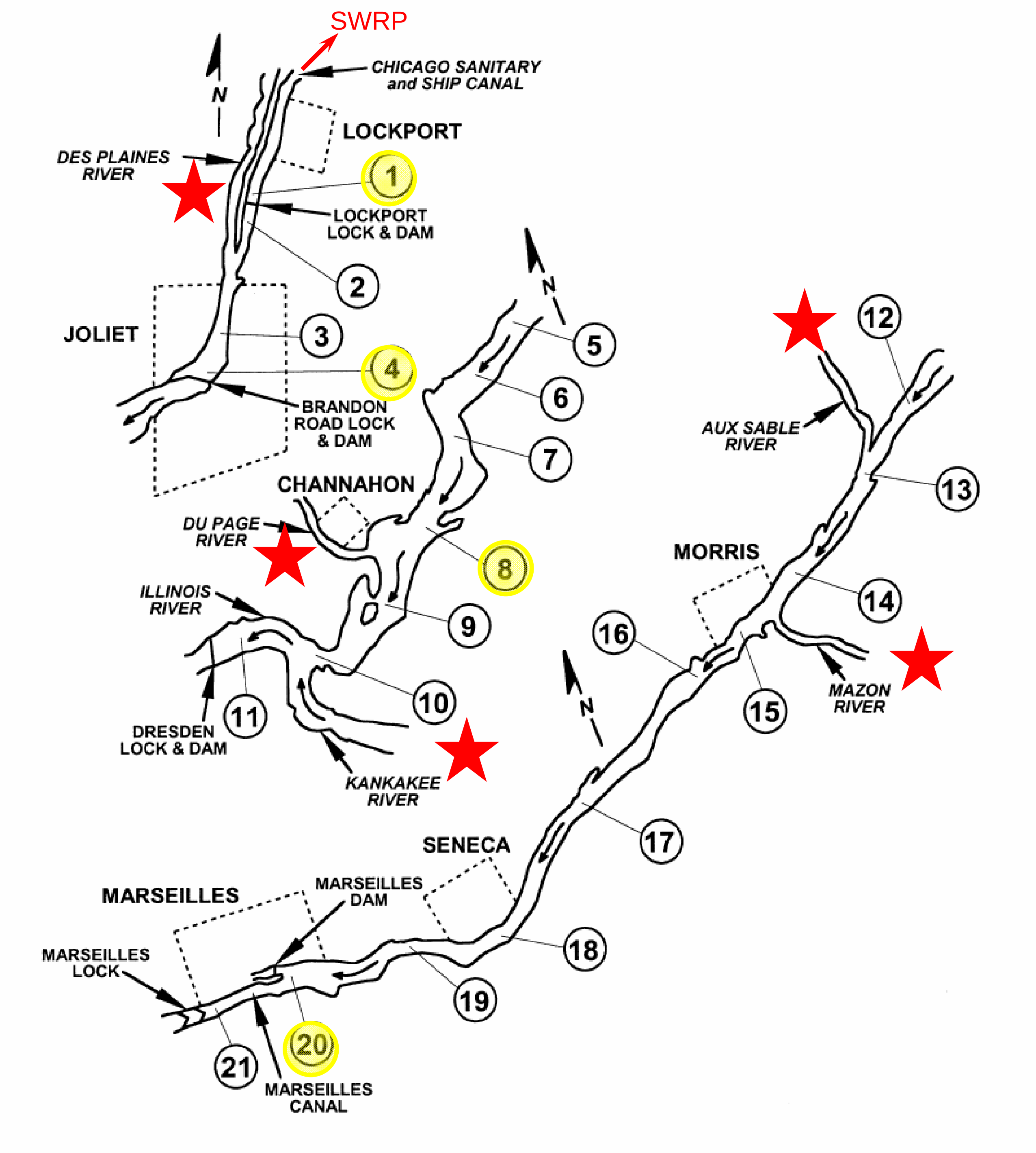
- Denitrification most effective during periods of low discharge.

Tributary sampling - 2008

- Undertaken to provide better constraints on sources of nitrate in Upper Illinois River watershed

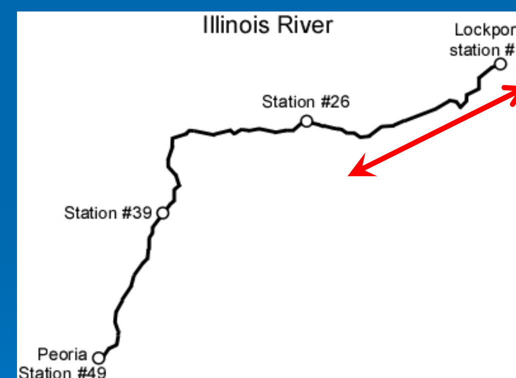
- Provides a more quantitative basis for numerical modeling

Upstream reach (Lockport to Marseilles)

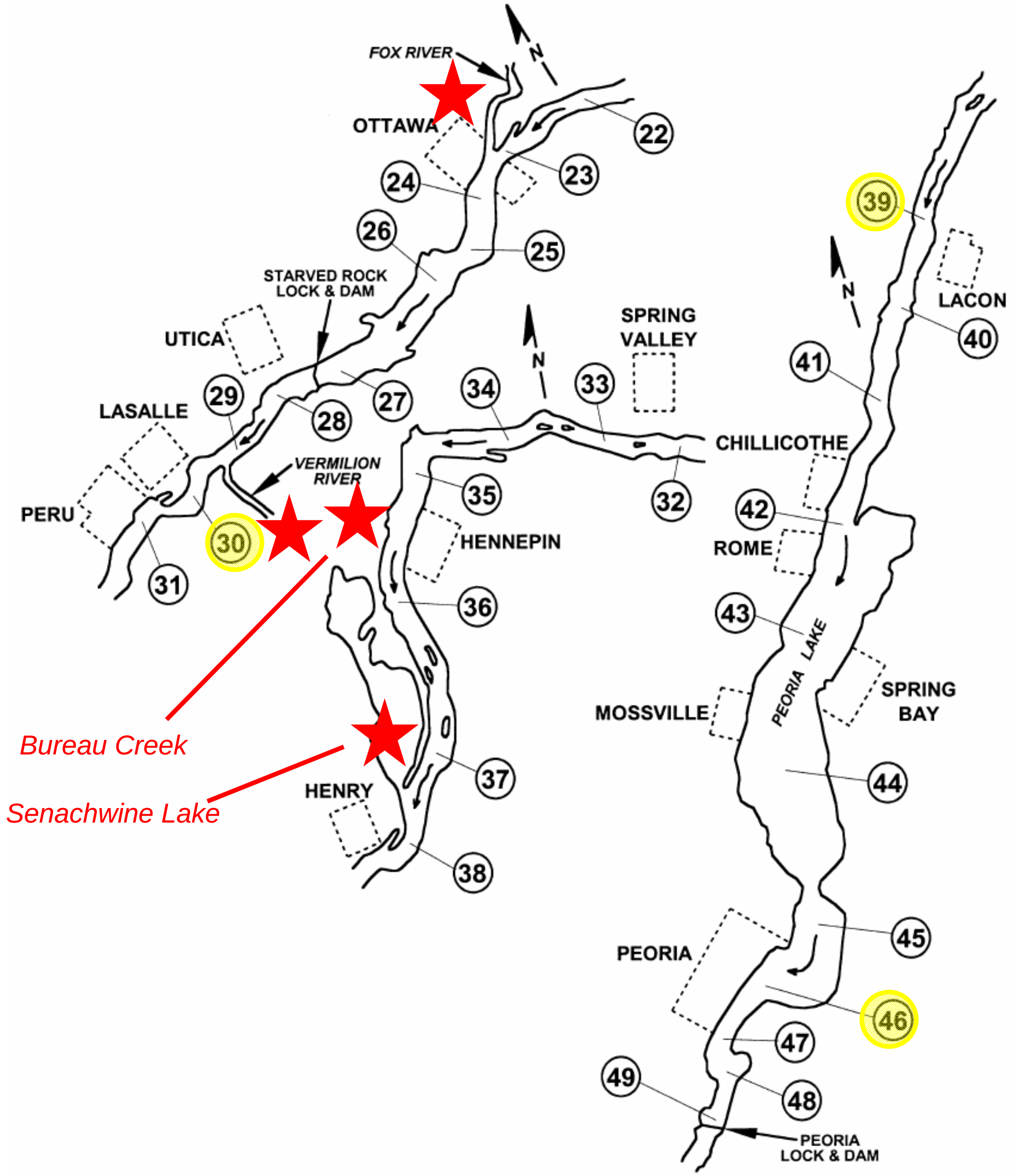


River sample

Tributary sample

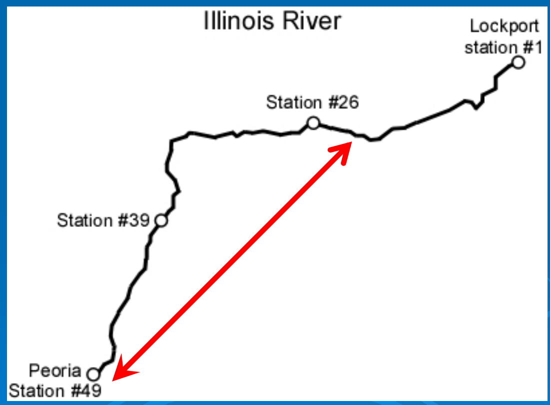


Downstream reach (Ottawa to Peoria)



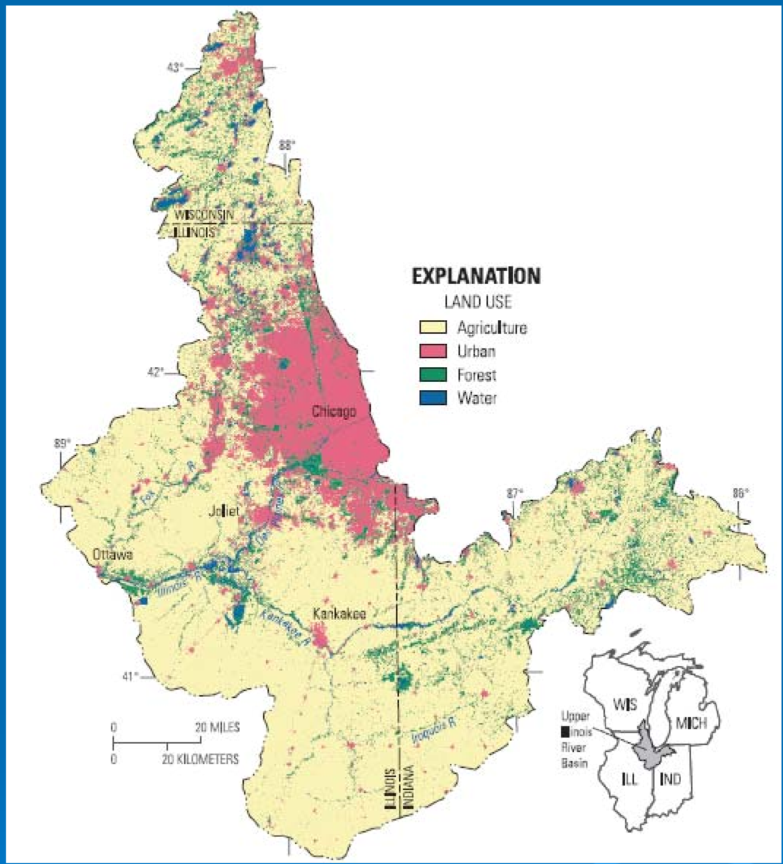
River sample

Tributary sample

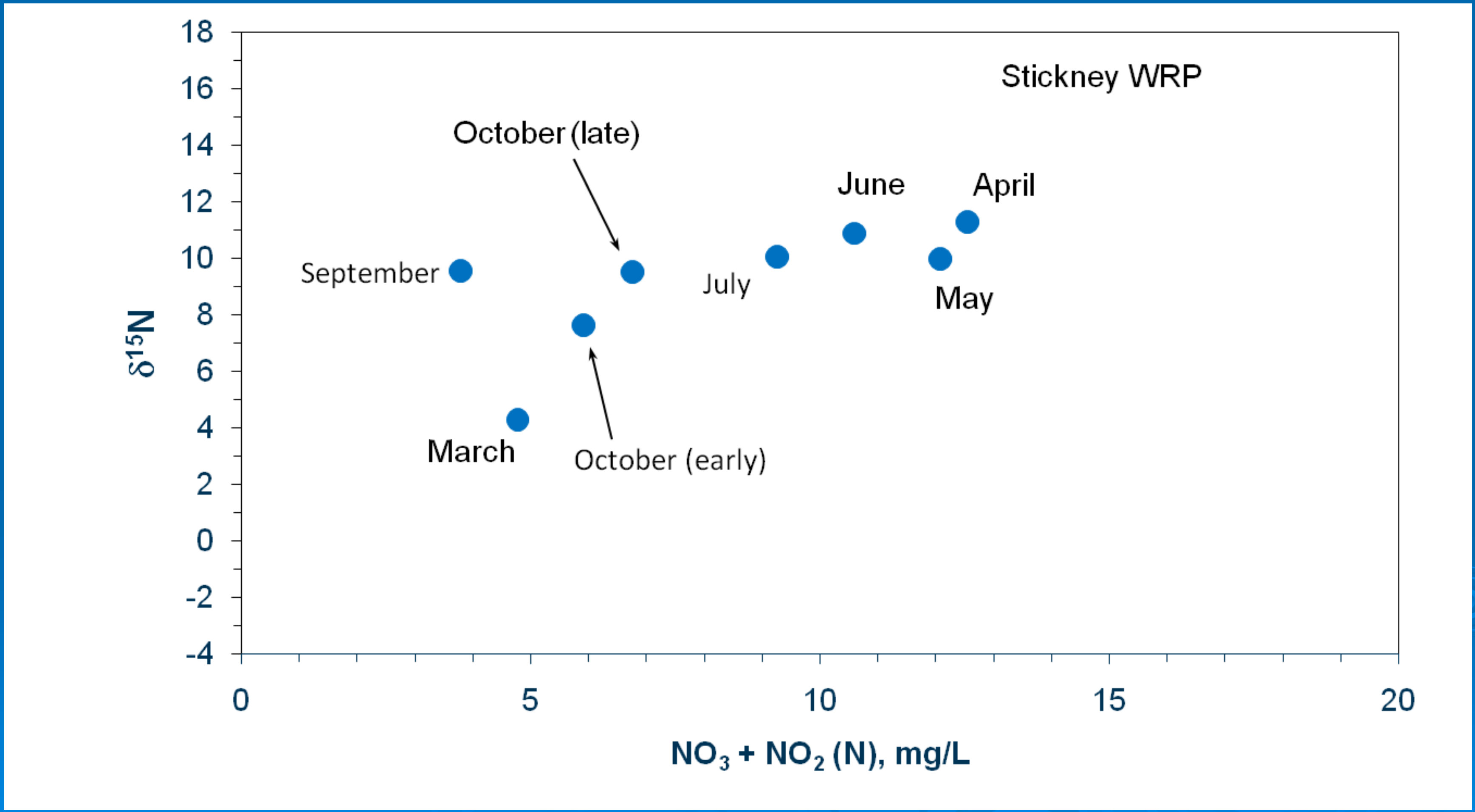


Tributary land use

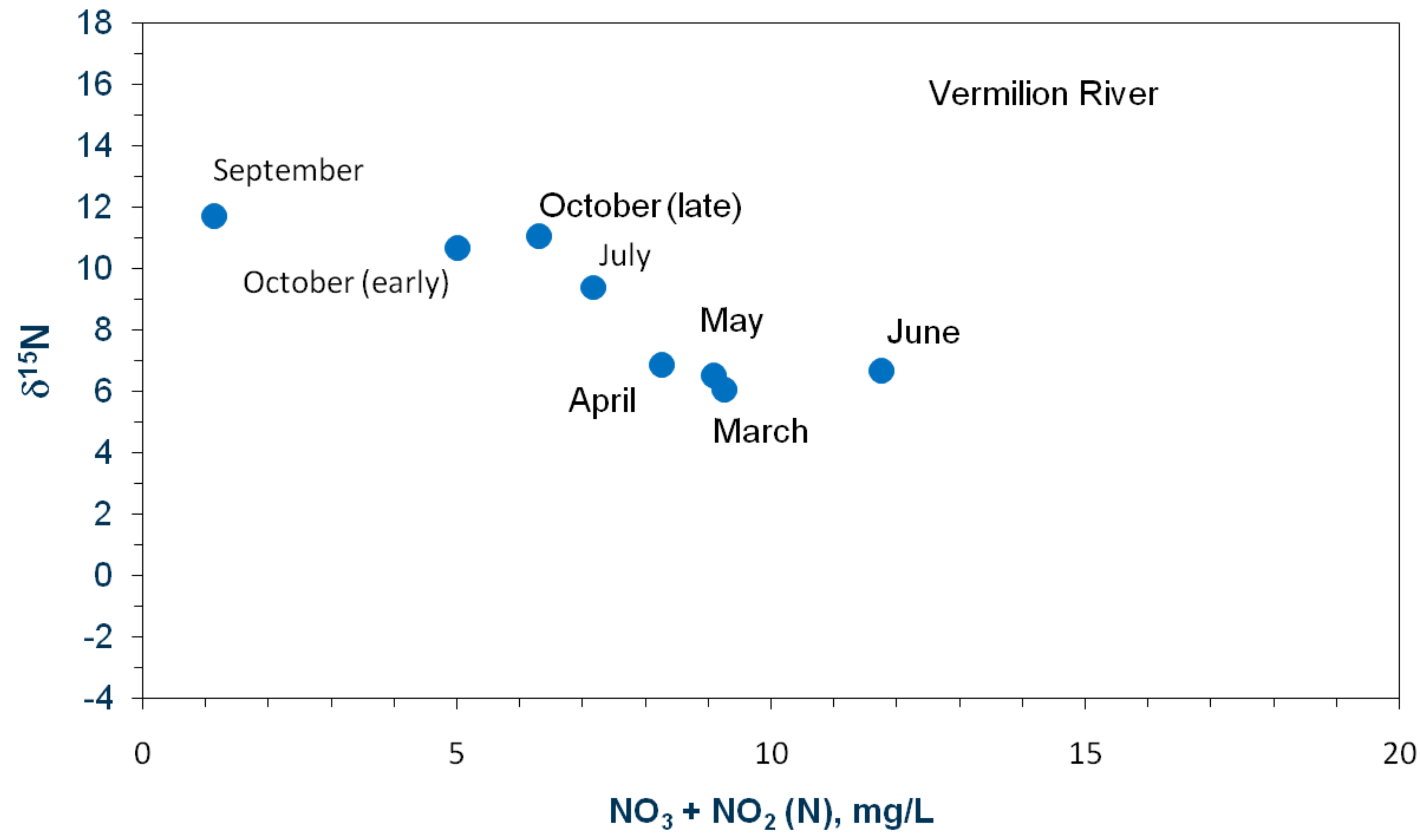
- Urban
  - SWRP
  - Des Plaines River
  - Du Page River
- Mixed Urban/Agricultural
  - Kankakee River
  - Fox River
- Agricultural
  - Aux Sable Creek
  - Mazon River
  - Vermilion River
  - Big Bureau Creek
  - Senachwine Lake (backwater)



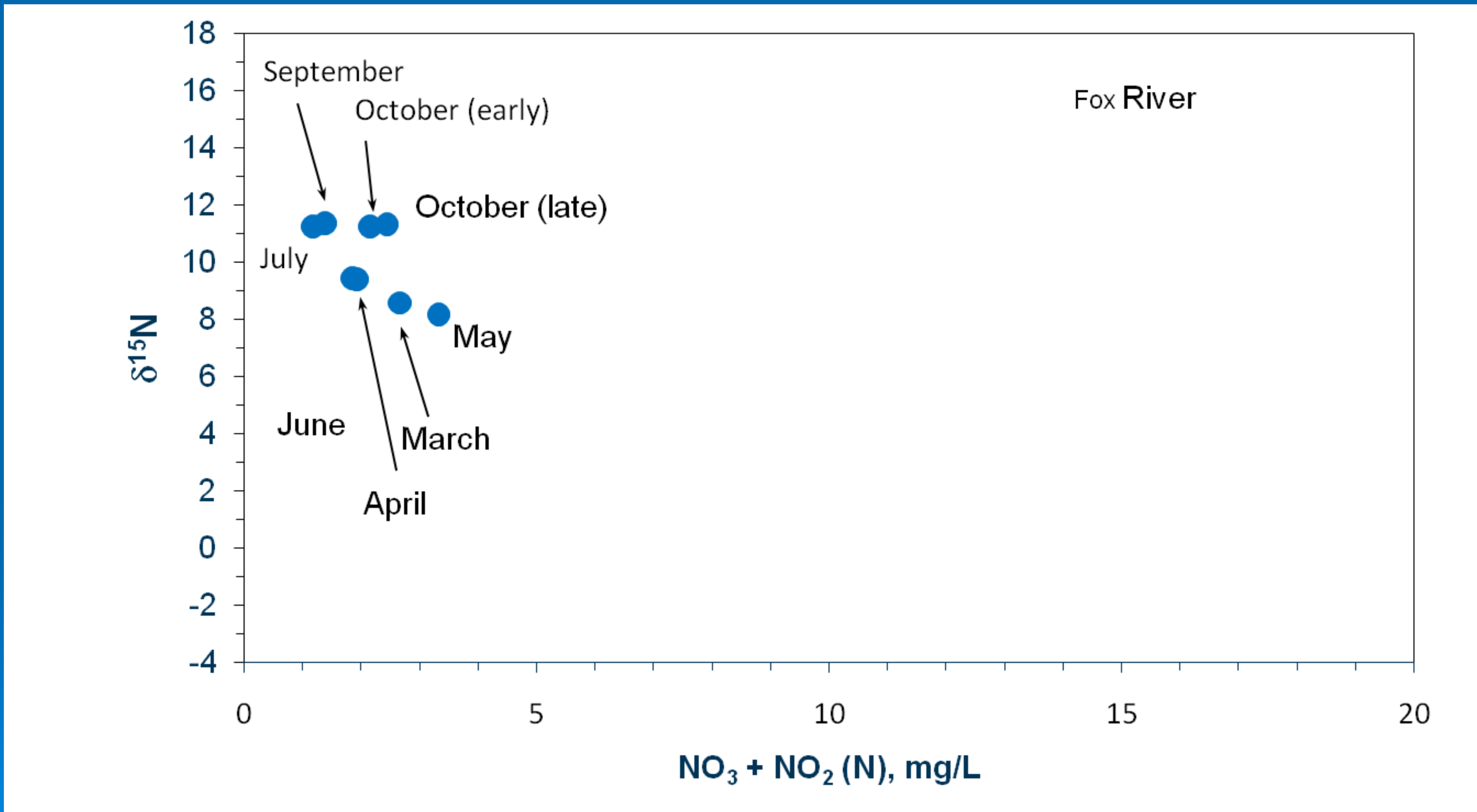
SWRP monthly 2008



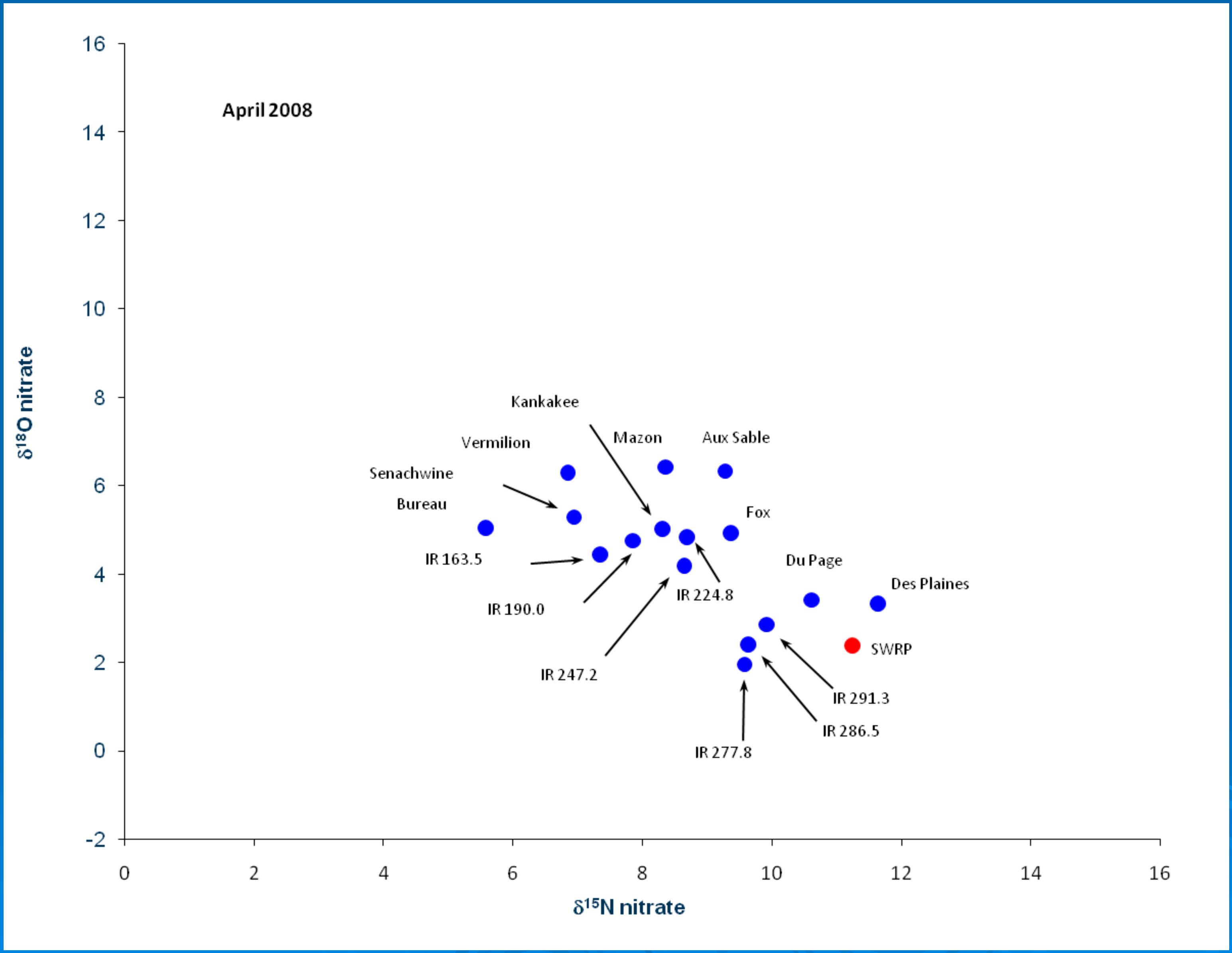
Vermilion River monthly 2008



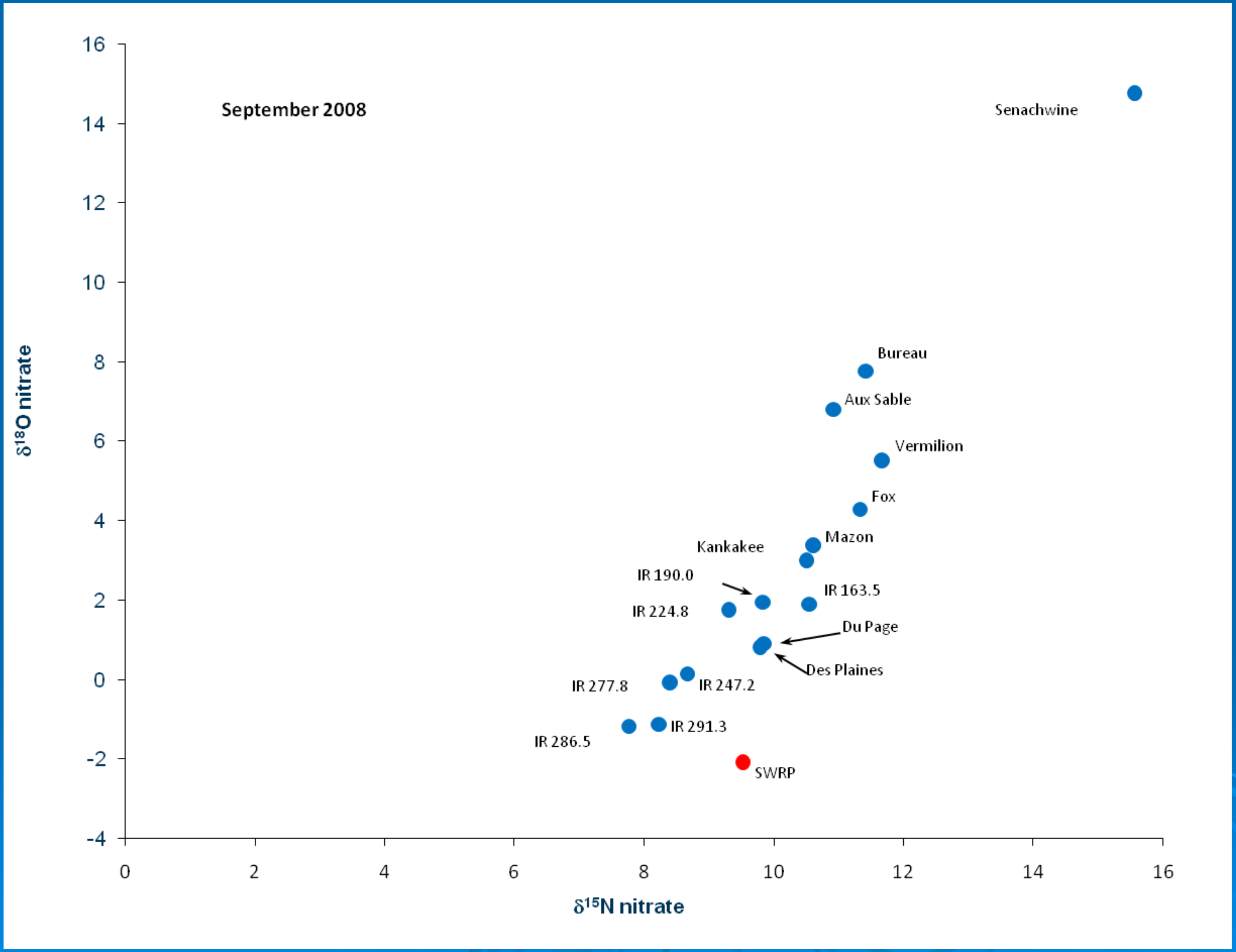
Fox River monthly 2008



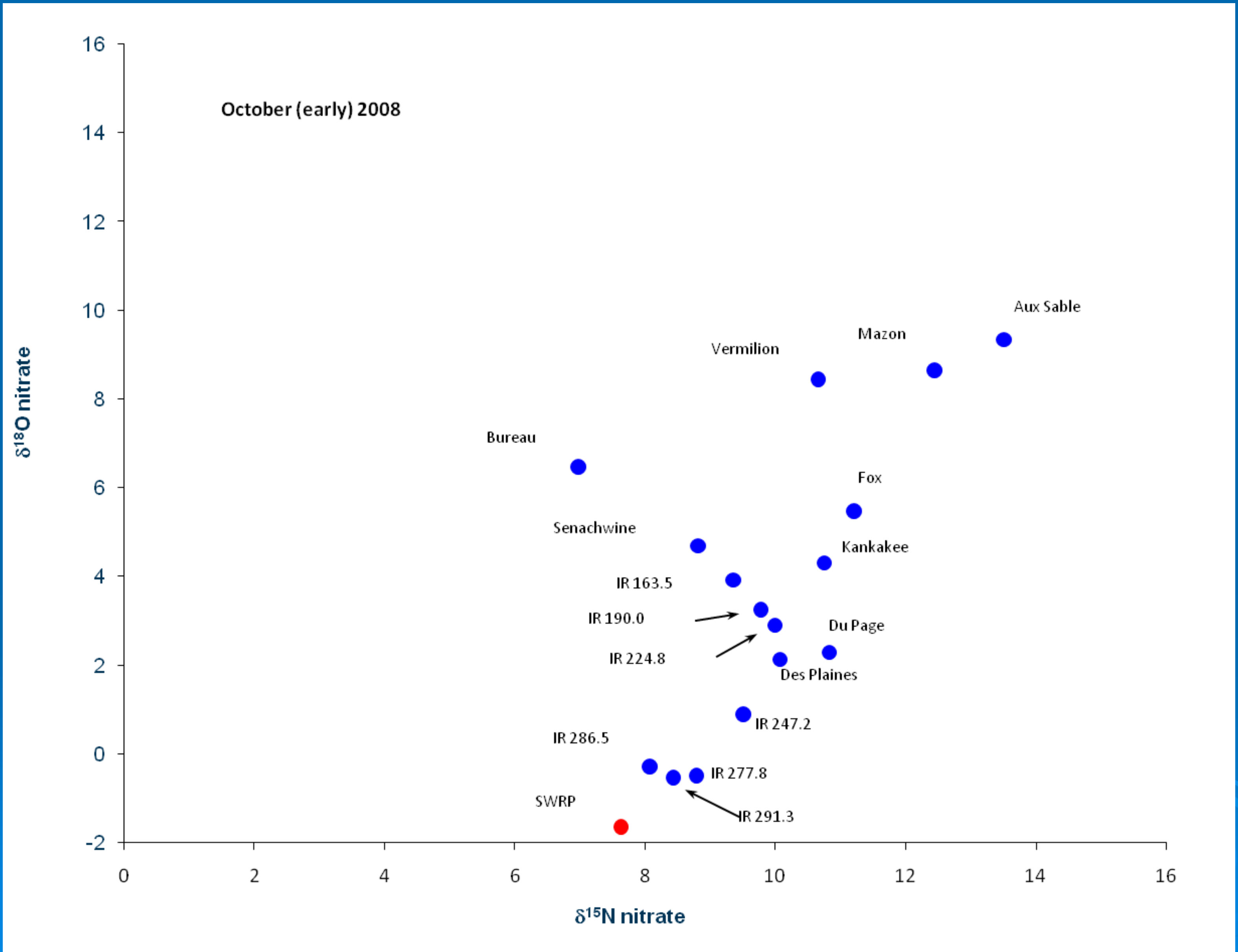
April 2008 – Nitrate isotopic data for all samples



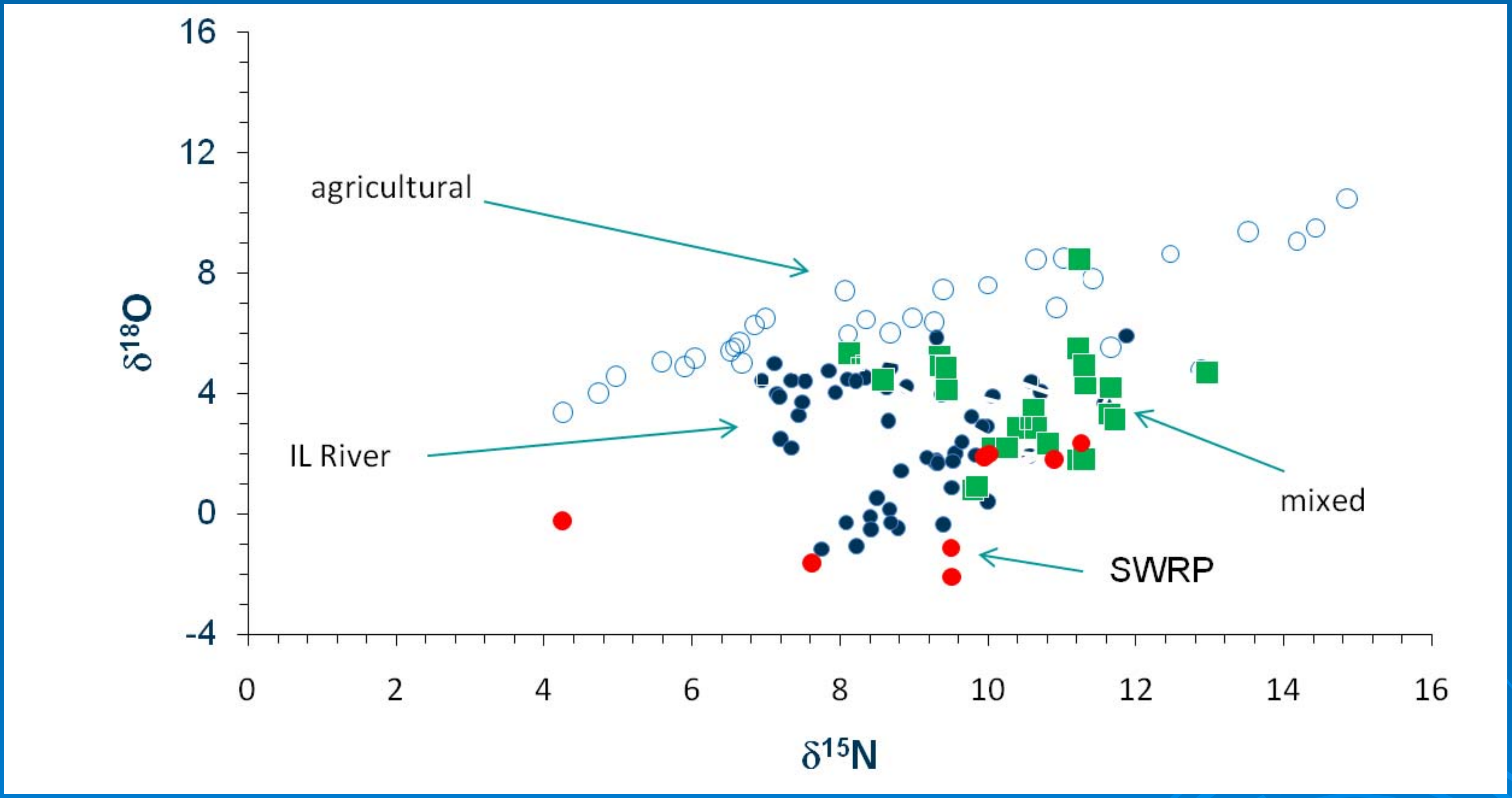
September 2008 – Nitrate isotopic data for all samples



October (early) 2008 – Nitrate isotopic data for all samples



Summary of 2008 nitrate isotopic data



Nitrate flux evaluations

- Daily fluxes estimated using nitrate concentration data and USGS discharge data
- Mass balance examined – do tributary fluxes sum to that observed in main river channel? If not, why not?
- Tributary flux divided by watershed area gives flux per unit area

Nitrate flux estimates (g/s)

	March	April	May	June	July	September
SWRP	125	288	314	264	254	205
ILWW #4	641	495	449	387	521	497
Du Page River	55	45	47	35	24	40
Kankakee River	852	408	424	565	214	56
Aux Sable Creek	24	14	30	32	1.4	0.9
Mazon River	52	35	45	35	11	2.5
sum	*1624*	*997*	*995*	*1054*	*771*	*596*
ILWW #20	1906	947	1061	1122	561	684
Δ%	*14.8*	*-5.3*	*6.2*	*6.1*	*-37*	*12.9*
Fox River	382	319	252	362	152	99
Vermilion River	268	174	163	222	117	6
Big Bureau Creek	47	60	59	116	145	2.4
sum	*2604*	*1500*	*1535*	*1822*	*975*	*791*
ILWW #39	3305	2215	2002	2466	2385	1154
Δ%	*21.2*	*32.3*	*23.3*	*35.3*	*59.1*	*31.4*
SWRP contribution:						
SWRP/ ILWW #20	6.6%	30.4%	29.6%	23.5%	45.2%	30.0%
SWRP/ ILWW #39	3.8%	13.0%	15.7%	10.7%	18.1%	17.8%

Areal nitrate fluxes by watershed 2008

(grams/hour/square mile)

	Drainage area (sq. mi.)	April	September
Du Page River	324	500	444
Kankakee River	5150	285	39
Aux Sable Creek	172	293	19
Mazon River	455	277	20
IL River @ Marseilles	8259	413	298
Fox River	2642	435	135
Vermilion River	1251	501	17
Big Bureau Creek	196	1102	44
IL River @ Henry	13544	589	307

Conclusions

- Isotopic compositions of nitrate give direct evidence of sources of nitrate within the Illinois Waterway and its tributary watersheds
- Relative proportions of nitrate sources can be estimated in terms of specific areal fluxes for individual watersheds
- Sufficient data exist to attempt numerical model at landscape scale